

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

EL 465677600

APPLICATION FOR LETTERS PATENT

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Methods of Forming Silicon Nitride, Methods of
Forming Transistor Devices, and Transistor
Devices

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INVENTOR

John T. Moore

ATTORNEY'S DOCKET NO. MI22-1374

EL 979977934

1 Methods of Forming Silicon Nitride, Methods of Forming
2 Transistor Devices, and Transistor Devices
3

4 TECHNICAL FIELD

5 The invention pertains to methods of forming silicon nitride, and
6 particularly pertains to methods of forming silicon nitride over silicon-
7 oxide-comprising materials. The invention also pertains to methods of
8 forming transistor devices, and further pertains to transistor device
9 structures.
10

11 BACKGROUND OF THE INVENTION

12 There are numerous semiconductor processing applications in which
13 it is desired to form a silicon-nitride-comprising layer over a silicon-
14 oxide-comprising layer. For instance, it can be desired to form transistor
15 devices having silicon nitride and silicon oxide as dielectric materials
16 between a conductive gate and a channel region. A difficulty in forming
17 silicon nitride over silicon oxide is described with reference to Figs. 1
18 and 2.

19 Referring initially to Fig. 1, a top view of a fragment of a
20 semiconductor structure is shown. Fragment 10 comprises an oxide
21 surface 12 upon which nitride 14 is to be formed. Oxide surface 12 can
22 comprise, for example, silicon dioxide; and nitride 14 can comprise, for
23 example, silicon nitride (Si_3N_4). The silicon nitride can be deposited by,

1 for example, chemical vapor deposition. A problem is that the silicon
2 nitride does not deposit readily on silicon dioxide, because there are only
3 a few bonds available for bonding of nitrogen to silicon in silicon
4 dioxide. Accordingly, the silicon nitride forms in small localized islands.
5 The islands grow, and eventually merge to form a silicon nitride
6 surface 14 that entirely covers silicon oxide 12. Such silicon nitride
7 surface is shown in Fig. 2.

8 The silicon nitride material that ultimately forms the surface of
9 Fig. 2 will typically be from about 30 to 35Å thick, and will frequently
10 be non-uniform in thickness as it was formed from the merger of
11 relatively thick islands (frequently the islands are about 28Å thick when
12 they merge) so that the portions where edges of the islands merged are
13 thinner than portions corresponding to centers of the islands. Further,
14 it can be difficult to control the overall thickness of nitride material 14,
15 as it is difficult to control how thick the islands of Fig. 1 will be when
16 they finally merge.

17 It would be desirable to develop new methods of forming silicon
18 nitride which overcome some or all of the above-discussed problems.
19

20 SUMMARY OF THE INVENTION

21 In one aspect, the invention encompasses a method of forming
22 silicon nitride on a silicon-oxide-comprising material. The silicon-oxide-
23 comprising material is exposed to activated nitrogen species from a

1 nitrogen-containing plasma to introduce nitrogen into an upper portion
2 of the material. The nitrogen is thermally annealed within the material
3 to bond at least some of the nitrogen to silicon proximate the nitrogen.
4 After the annealing, silicon nitride is chemical vapor deposited on the
5 nitrogen-containing upper portion of the material.

6 In another aspect, the invention encompasses a method of forming
7 a transistor device. A silicon-oxide-comprising layer is formed over a
8 substrate. The silicon-oxide-comprising layer is exposed to activated
9 nitrogen from a nitrogen-containing plasma to introduce nitrogen into an
10 upper portion of the layer. The nitrogen is thermally annealed within
11 the layer to bond at least some of the nitrogen to silicon proximate the
12 nitrogen. After the annealing, silicon nitride is chemical vapor deposited
13 on the nitrogen-containing upper portion of the layer. At least one
14 conductive gate layer is formed over the silicon nitride, and defines a
15 gate layer. A pair of source/drain regions are formed proximate the
16 gate layer and gatedly connected to one another through a channel
17 region that is beneath the gate layer.

18 In yet another aspect, the invention encompasses transistor device
19 structures.

20 21 BRIEF DESCRIPTION OF THE DRAWINGS

22 Preferred embodiments of the invention are described below with
23 reference to the following accompanying drawings.

1 Fig. 1 is a diagrammatic, fragmentary, top view of a semiconductor
2 wafer fragment at a preliminary step of a prior art processing sequence.

3 Fig. 2 is a view of the Fig. 1 wafer fragment shown at a prior art
4 processing step subsequent to that of Fig. 1.

5 Fig. 3 is a diagrammatic, cross-sectional view of a semiconductor
6 wafer fragment at a preliminary step of a method of the present
7 invention.

8 Fig. 4 is a view of the Fig. 3 wafer fragment shown at a
9 processing step subsequent to that of Fig. 3.

10 Fig. 5 is a view of the Fig. 3 wafer fragment shown at a
11 processing step subsequent to that of Fig. 4.

12 Fig. 6 is a view of the Fig. 3 wafer fragment shown at a
13 processing step subsequent to that of Fig. 5.

14 Fig. 7 is a view of the Fig. 3 wafer fragment shown at a
15 processing step subsequent to that of Fig. 6.

16 Fig. 8 is a diagrammatic, cross-sectional view of an apparatus which
17 can be utilized in methodology of the present invention.

18 Fig. 9 is a diagrammatic, cross-sectional view of another apparatus
19 which can be utilized in methodology of the present invention.
20
21
22
23

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

A method of the present invention is described with reference to Figs. 3-9.

Referring initially to Fig. 3, a wafer fragment 20 is illustrated. Fragment 20 comprises a substrate 16 having an oxide layer 18 formed thereover. Substrate 16 can comprise, for example, a bulk semiconductive material substrate such as, for example, monocrystalline silicon lightly doped with a background p-type dopant. To aid in interpretation of the claims that follow, the terms "semiconductive substrate" and "semiconductor substrate" are defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

Oxide layer 18 can be formed over substrate 16 by, for example, chemical vapor deposition of silicon dioxide. Alternatively, oxide layer 18 can correspond to a thin layer of native oxide resulting from exposure

1 of substrate 16 to air or other sources of oxygen. If layer 18
2 corresponds to native oxide, it can correspond to a layer less than or
3 equal to approximately 5Å thick, and comprising silicon dioxide. Layer
4 18 can also consist essentially of silicon dioxide, or consist of silicon
5 dioxide. In particular embodiments of the invention, layer 18 can have
6 a thickness of from about 1Å to about 50Å, such as, for example, a
7 thickness of about 40Å.

8 Fig. 4 illustrates a nitrogen-comprising region 22 being formed on
9 and/or within oxide layer 18. Nitrogen-comprising region 22 is a thin
10 layer formed by exposing silicon-oxide comprising material 18 to an
11 activated nitrogen species formed from a nitrogen-containing plasma, with
12 the term "activated" indicating that the nitrogen species is different than
13 the form of nitrogen fed to the plasma. An activated nitrogen species
14 can comprise, for example, a nitrogen ion or a nitrogen atom in an
15 energy state higher than its ground state.

16 An exemplary method of providing nitrogen within oxide layer 14
17 is to expose layer 18 to a nitrogen-containing plasma and thereby
18 introduce nitrogen into layer 18. Such introduction forms nitrogen-
19 enriched upper region 22 of layer 18 and leaves a non-nitrogen-enriched
20 region beneath the nitrogen-enriched upper region. The nitrogen-
21 enriched upper portion of oxide layer 18 can be formed within the top
22 2Å of layer 18. If oxide layer 18 is less than or equal to about 5Å
23 thick, nitrogen-enriched upper portion 22 preferably does not extend

1 below the top half of layer 18. If oxide layer 18 is at least 10Å thick,
2 nitride-enriched portion 22 is preferably at least about 5Å above
3 substrate 16, and more preferably only within the top 5Å of layer 18.
4 It can be advantageous to keep the nitrogen above an upper surface of
5 substrate 16 to avoid having the nitrogen migrate into upper surface 16
6 and disrupt operation formed in and/or over a surface of substrate 16.
7 It is to be understood, however, that the invention encompasses
8 embodiments wherein nitrogen migration into a surface of substrate 16
9 is acceptable, and in such embodiments the nitrogen-enriched portion of
10 layer 18 can extend throughout an entirety of layer 18.

11 The nitrogen-containing plasma can be formed from, for example,
12 N₂, NH₃ and/or N₂O. The plasma can be predominantly composed of
13 nitrogen-containing species, consist essentially of nitrogen-containing
14 species, or consist entirely of nitrogen-containing species. In exemplary
15 embodiments, layer 18 is maintained at a temperature of less than or
16 equal to 200°C during the exposure to the nitrogen-containing plasma.
17 Such can alleviate diffusion of nitrogen into a lower half of oxide
18 layer 18. Particular exemplary temperatures can be from 50°C to 200°C,
19 with a suitable temperature being about 65°C. The nitrogen-containing
20 plasma can be maintained with a power of from about 500 watts to
21 about 5,000 watts during exposure of layer 18 to the plasma, and in
22 particular embodiments can be maintained with a power of from about
23 500 watts to about 3,000 watts during the exposing. A pressure within

1 a reaction chamber comprising the plasma and oxide layer 18 can be less
2 than 3 Torr. The time of exposure of layer 14 to the nitrogen-
3 containing plasma is preferably for a time of less than or equal to about
4 1 minute, and in particular embodiments can be for a time of from
5 about 3 seconds to about 1 minute. An exemplary process utilizes an
6 exposure time of from about 10 seconds to about 15 seconds.

7 Figs. 8 and 9 illustrate exemplary apparatuses which can be
8 utilized for forming nitrogen-comprising region 22.

9 Referring initially to Fig. 8, a remote plasma nitridization
10 apparatus 200 is illustrated. Apparatus 200 comprises a plasma
11 chamber 202 and a reaction chamber 204. Reaction chamber 204
12 comprises a substrate holder 206, and substrate 16 is supported within
13 chamber 204 by holder 206. Preferably, holder 206 is configured to
14 rotate substrate 16 during exposure of substrate 16 to activated nitrogen
15 species. Such activated nitrogen species are formed within plasma
16 chamber 202 by, for example, exposing N_2 and/or other nitrogen-
17 containing materials (such as N_2O or NH_3) to plasma conditions.
18 Exemplary plasma conditions comprise utilization of a microwave plasma
19 generator at a power of from about 1,500 watts to about 3,000 watts,
20 and utilizing a pressure within chamber 202 of less than 3 Torr. The
21 plasma of chamber 202 forms activated nitrogen species which migrate
22 along a passageway 208 into chamber 204 whereupon the species can
23

1 form nitrogen-comprising layer 22 (Fig. 4) over and/or within oxide 18
2 (Fig. 4).

3 An arrow is shown within passageway 208 to indicate migration of
4 plasma activated nitrogen species through passageway 208. Preferably,
5 passageway 208 is of sufficient length so that plasma 202 is at least
6 about 12 inches from substrate 16. Such can enable highly activated
7 nitrogen species formed within a plasma to relax prior to interaction with
8 substrate 16, which can limit penetration of the nitrogen species into
9 substrate 16 relative to an amount of penetration which would occur with
10 more highly activated species. In order to further limit penetration of
11 nitrogen species into substrate 16, substrate 16 is preferably not biased
12 relative to the plasma within chamber 202.

13 Suitable operating conditions for forming a nitrogen-comprising
14 plasma over substrate 16 can include maintaining a temperature of
15 substrate 16 at from about 550°C to about 1,000°C, rotating the wafer
16 comprising substrate 16 at about 90 rotations per minute (RPM),
17 maintaining a pressure within chambers 202 and 204 of from about
18 0.8 Torr to about 2.8 Torr, and exposing the wafer to the nitridization
19 conditions for from about one minute to about five minutes.

20 Referring next to Fig. 9, an alternative apparatus which can be
21 utilized for forming nitrogen over and within oxide layer 18 (Fig. 4) is
22 illustrated as apparatus 220. Apparatus 220 can be referred to as a
23 high density plasma remote plasma nitridization (HDP-RPN) apparatus,

1 or simply as a plasma nitridization (PN) apparatus. Apparatus 220
2 comprises a reaction chamber 222 having a wafer holder 224 therein.
3 Wafer 16 is supported on holder 224. A plasma 226 is formed above
4 substrate 16, and preferably is maintained a distance "X" from
5 substrate 16, with distance "X" corresponding to at least about four
6 inches. Nitrogen is introduced into plasma 226 in the form of, for
7 example, N_2 , and activated nitrogen species are formed from the
8 nitrogen. Suitable processing parameters for utilization of the apparatus
9 of Fig. 9 include a wafer temperature of from 0°C to 400°C, no rotation
10 of the substrate 16, a pressure within chamber 222 of from about
11 5 mTorr to about 15 mTorr (preferably of from about 5 mTorr to
12 about 10 mTorr), and an exposure time of substrate 16 to activated
13 nitrogen species within chamber 222 of from about 5 seconds to
14 about 30 seconds.

15 The plasma treatment described above with reference to Figs. 8
16 and 9 preferably forms a minimum of about 5% nitrogen within the
17 upper surface silicon dioxide of layer 18. The nitrogen formed within
18 such upper surface is then thermally annealed to bond at least some of
19 the nitrogen, and preferably all of the nitrogen, to silicon proximate the
20 nitrogen. The thermal bonding of the nitrogen alleviates diffusion of the
21 nitrogen through layer 18 (Fig. 4) and into substrate 16 (Fig. 4). The
22 annealing can comprise thermal processing at a temperature of less than
23 1,100°C for a time of at least 3 seconds, and can comprise, for example,

1 a temperature of 700°C for at time of about 30 seconds, or 1,050°C for
2 a time of about 5 seconds. Alternatively, the annealing can comprise
3 rapid thermal processing (RTP) utilizing a ramp rate of at least
4 50°C/second to a temperature of less than 1,000°C, with such
5 temperature being maintained for at least about 30 seconds. Suitable
6 processing can include a temperature of about 900°C for at time of
7 about 60 seconds.

8 After the thermal annealing of the nitrogen, the nitrogen of the
9 nitrogen-enriched upper portion of oxide layer 18 can be entirely within
10 the top 5Å of layer 18. More specifically, if oxide layer 18 is at least
11 10Å thick, the nitride-enriched portion is preferably at least about 5Å
12 above substrate 16, and more preferably only within the top 5Å of layer
13 18 after the thermal annealing of the nitrogen. It can be advantageous
14 to keep the nitrogen above an upper surface of substrate 16 to avoid
15 having the nitrogen migrate into upper surface 16 and disrupt operation
16 of a channel region ultimately formed in substrate 16. It is to be
17 understood, however, that the invention encompasses embodiments
18 wherein nitrogen migration into a surface of substrate 16 is acceptable,
19 and in such embodiments the nitrogen-enriched portion of layer 18 can
20 extend throughout an entirety of layer 18 after the thermal annealing.

21 Referring to Fig. 5, a layer 24 of silicon nitride is chemical vapor
22 deposited over nitrogen-enriched portion 22 of silicon dioxide layer 18.
23 An exemplary process for the chemical vapor deposition of silicon nitride

1 includes utilization of NH_3 and dichlorosilane as silicon nitride
2 precursors, a temperature of from about 600°C to about 800°C , a
3 pressure of from about 0.1 Torr to about 2 Torr, and a time of from
4 about 10 minutes to about 100 minutes. Silicon-enriched portion 22
5 provides a surface upon which silicon nitride (for example, Si_3N_4) can be
6 uniformly and controllably deposited. Layer 24 can thus be deposited
7 to have a substantially planar upper surface, and accordingly a uniform
8 thickness throughout. Further, the final thickness of layer 24 can be
9 controllably determined. Preferably, layer 24 is formed to a thickness
10 of from about 30\AA to about 50\AA , and in an exemplary embodiment is
11 formed to a thickness of about 40\AA over a 5\AA thick silicon dioxide layer
12 18. In one aspect of the present invention, layers 18, 22 and 24 are
13 utilized as a dielectric material beneath a transistor gate. Preferably,
14 such dielectric material will provide a drive current comparable to that
15 provided by a conventional gate oxide layer (i.e., by a gate dielectric
16 material that consists essentially of silicon dioxide). Conventional gate
17 oxide layers are typically from about 35\AA thick to about 50\AA thick.
18 Since silicon nitride has a higher dielectric constant than silicon dioxide,
19 the dielectric material corresponding to layers 24, 22 and 18 will be
20 formed thicker than a dielectric material consisting of silicon dioxide to
21 have the same drive current as the material consisting of silicon dioxide.
22 For instance, in an embodiment in which silicon dioxide layer 18 has a
23 thickness of about 10\AA , layer 22 has a negligible thickness (i.e., less than

1 about 5Å), and layer 24 has a thickness of about 40Å; the composite
2 layer formed from materials 18, 22 and 24 can be utilized in a transistor
3 to accomplish a drive current corresponding approximately to that of a
4 35Å thick dielectric material consisting of silicon dioxide.

5 An advantage of utilizing silicon nitride within a gate dielectric
6 material is that the silicon nitride enables the gate dielectric material to
7 be thicker than if the material consisted of silicon dioxide, and yet to
8 accomplish the same drive current as a dielectric material consisting of
9 silicon dioxide. The thicker layer will be less affected by minor
10 variations in thickness than would a thin layer. Accordingly, utilization
11 of a thicker dielectric material comprising silicon nitride relative to a
12 thinner material consisting of silicon dioxide can reduce tolerances of
13 semiconductor processing steps, and accordingly reduce instances of device
14 failure.

15 Figs. 6 and 7 illustrate methodology for forming a transistor device
16 incorporating the composite dielectric material of layers 18, 22 and 24.
17 Referring to Fig. 6, layers 26, 28 and 30 are formed over layer 24.
18 Layers 26, 28 and 30 can correspond to, for example, conductively doped
19 silicon, metal silicide, and insulative dielectric materials, respectively.
20 More specifically, layer 26 can correspond to conductively doped silicon
21 which is doped with either n-type or p-type dopant, and can correspond
22 to, for example, conductively doped polycrystalline silicon or conductively
23 doped amorphous silicon. Layer 28 can correspond to, for example,

1 titanium silicide or tungsten silicide, and layer 30 can correspond to
2 silicon nitride or silicon dioxide.

3 Referring to Fig. 7, layers 18, 22, 24, 26, 28 and 30 are patterned
4 into a gate structure of a transistor device 50. Layers 18, 22 and 24
5 correspond to a dielectric material under conductive gate material 26,
6 and a channel region is defined to be beneath conductive material 26
7 and in the semiconductive material of substrate 16.

8 Lightly doped diffusion regions 40 are formed within substrate 16
9 and proximate the channel region. Lightly doped diffusion regions 40
10 can comprise either n-type dopant or p-type depending on the type of
11 transistor device 50 (i.e., depending on whether the transistor device 50
12 corresponds to a PMOS or NMOS transistor).

13 Sidewall spacers 42 are formed adjacent sidewalls of the gate
14 structure, and over lightly doped diffusion regions 40. Sidewall
15 spacers 42 can be formed by conventional methods, such as, for example,
16 by depositing an insulative material over substrate 16 and subsequently
17 anisotropically etching the insulative material to define spacers 42. A
18 suitable insulative material for spacers 42 is either silicon nitride or
19 silicon dioxide.

20 Heavily doped source/drain regions 44 are formed within
21 substrate 16, and are formed to be gatedly connected by the gate
22 comprising conductive materials 26 and 28. Source/drain regions 44 can
23 be more heavily doped with either n-type dopant or p-type dopant,

1 depending on whether device 50 is to be an NMOS device or a PMOS
2 device. Heavily doped regions 44 will typically comprise at least
3 1×10^{19} atoms/cm³ of conductivity enhancing dopant.

4 The relative thicknesses of 18, 22, 24, 26, 28 and 30 are shown
5 diagrammatically, and not in proportion to the thicknesses of such layers
6 in actual devices. In particular devices, layer 18 can comprise a
7 thickness less than or equal to about 10Å, and can, for example,
8 comprise a thickness of less than or equal to about 5Å. Layer 22 will
9 have a negligible thickness, and will be formed within an upper portion
10 of layer 18. Layer 22 can, for example, comprise a thickness of from
11 about 1Å to about 2Å. Silicon nitride layer 24 can comprise a thickness
12 of greater than or equal to 30Å, and in particular embodiments will
13 comprise a thickness of at least about 40Å, and can, for example,
14 comprise a thickness of at least about 50Å.

15 In compliance with the statute, the invention has been described
16 in language more or less specific as to structural and methodical
17 features. It is to be understood, however, that the invention is not
18 limited to the specific features shown and described, since the means
19 herein disclosed comprise preferred forms of putting the invention into
20 effect. The invention is, therefore, claimed in any of its forms or
21 modifications within the proper scope of the appended claims
22 appropriately interpreted in accordance with the doctrine of equivalents.
23